Crystals and diffraction

The scattering of small particles from periodic surfaces gives rise to diffraction, similar to the case in bulk crystals. The only difference is that now the periodicity exists only in the x-y plane of the surface, and not along the normal direction z. Diffraction can be used to determine the structure of the surface, provided we know the interaction potential between the particle and the surface and we can solve the Schrödinger equation. In principle any particle will give rise to diffracted beams if the wavelength is comparable to the lattice parameter ~2-5 Å.

The wavelength λ is:

For electrons, neutrons and atoms: momentum $p = h/\lambda$ → $\lambda = \dfrac{h}{\sqrt{2mE}}$

For photons: $c = \lambda \nu$, $E = h\nu$ → $\lambda = hc/E$

Where c = speed of light, h = Planck constant, ν = frequency. To get wavelengths of ~2-5 Å the energies E should be around

For electrons	> 40 eV
Atoms, protons and neutrons	25 meV
X-rays	2-6 keV

To make the technique useful for structure determination the interaction should be sensitive to the surface. That excludes neutrons and hard X-rays, since they penetrate deep into the sample and the surface represents only a small fraction of scatterers.

There are special ways to use these more penetrating particles, for example using powder materials for neutrons, where the surface area is increased enormously. For X-rays one can resort to grazing angles <10º for 5 KeV photons and less than 1-2º for 100 KeV photons.

The most popular technique for surface studies is Low Energy Electron Diffraction or LEED, which uses electrons of ~100 eV. This has the advantage that the penetration depth of elastically scattered electrons into the sample is very small, one or two atomic layers and therefore surface sensitivity is assured. Unfortunately these advantages make interpretation of diffracted intensities difficult, since the short mean free path, which is the key to its surface sensitivity, implies strong interaction, and therefore multiple scattering events. Another technique is He atom scattering. Helium at thermal energies does not penetrate the surface. In fact the atoms bounce off the surface at relatively large distances from the nuclei of the first layer of surface atoms.

Crystal structures have been studied for many years by means of *diffraction*. Diffraction is the phenomenon by which radiation (x-ray, electron, neutron, etc.) is deflected by the atoms and electrons constituting the crystal in specific directions. It is the result of constructive and destructive interference of the scattered waves at the detector, far away from the crystal.

Photon and electron waves propagating in free space

In free space the radiation propagates as plane waves, which can be represented by the wavefunction:

$$\Psi(\mathbf{r},t) = \psi_o.e^{i(\mathbf{k.r} - \omega t)}$$

Where: $\mathbf{k.r} - \omega t$ = phase, ψ_o = maximum amplitude, $\mathbf{k}$ = wave vector, ω = angular frequency = $2\pi\nu$

For electrons: $\lambda(\text{Å}) = 12/\sqrt{E(eV)}$. Therefore for E = 100 eV, λ = 1.2 Å

For photons : $\lambda(\text{Å}) = 12.4/ E(KeV)$. For E = 10,000 eV, λ = 1.24 Å

In all the following all vector quantities will be represented either by bold symbols of by a small arrow on top of the symbol. The same symbol in plain character is the modulus or length of the vector, for example: $k = |\mathbf{k}| = |\overrightarrow{k}|$

The Davisson–Germer experiment

It was a physics experiment conducted by American physicists Clinton Davisson and Lester Germer in 1927.
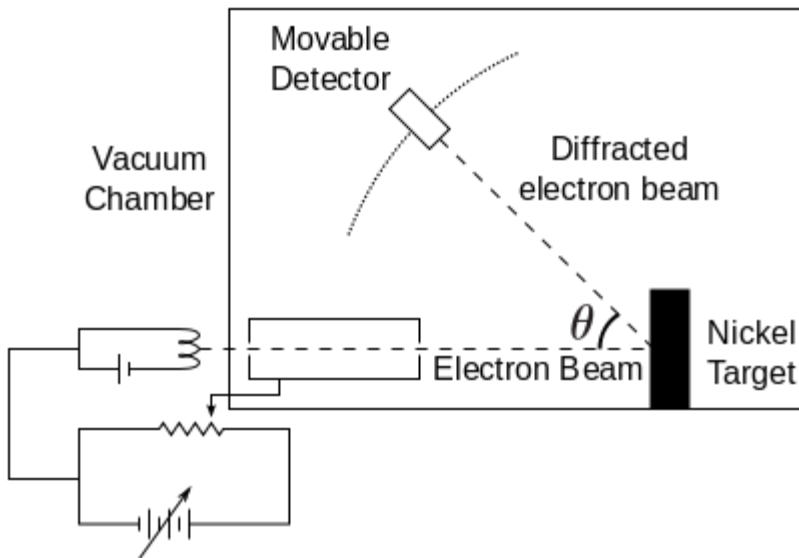
Davisson and Germer's objective was to study the surface of a piece of nickel by directing a beam of electrons at the surface and observing how many electrons bounced off at various angles. To avoid collisions of the electrons with other molecules on their way towards the surface, the experiment was conducted in a vacuum chamber.
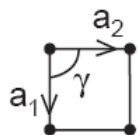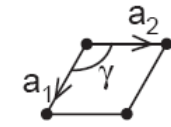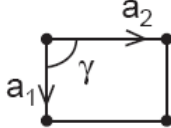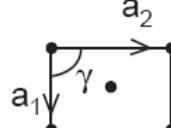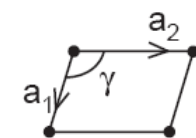During the experiment an accident occurred and air entered the chamber, producing an oxide film on the nickel surface. To remove the oxide, Davisson and Germer heated the specimen in a

high temperature oven, not knowing that this affected the formerly polycrystalline structure of the nickel to form large single crystal areas with crystal planes continuous over the width of the electron beam.

When they started the experiment again and the electrons hit the surface, they were scattered by atoms which originated from crystal planes inside the nickel crystal. As Max von Laue proved in 1912 the crystal structure serves as a three dimensional diffraction grating.

Bravais lattice:

A collection of periodically spaced points in 3 dimensional space. Crystals can be thought of as a Bravais lattice with each point substituted by an atom, ion, molecule or groups of these. The 5 Bravais lattices in two dimensions are:

	square	$a_1 = a_2$	$\gamma = 90°$
	hexagonal	$a_1 = a_2$	$\gamma = 120°$
	rectangular	$a_1 \neq a_2$	$\gamma = 90°$
	centered rectangular	$a_1 \neq a_2$	$\gamma = 90°$
	oblique	$a_1 \neq a_2$	$\gamma \neq 90°, 120°$

Reciprocal lattice:

A reciprocal lattice of a Bravais lattice is generated by all the wave vectors **K** of waves that have the same phase in each and every point of the Bravais lattice. Example:
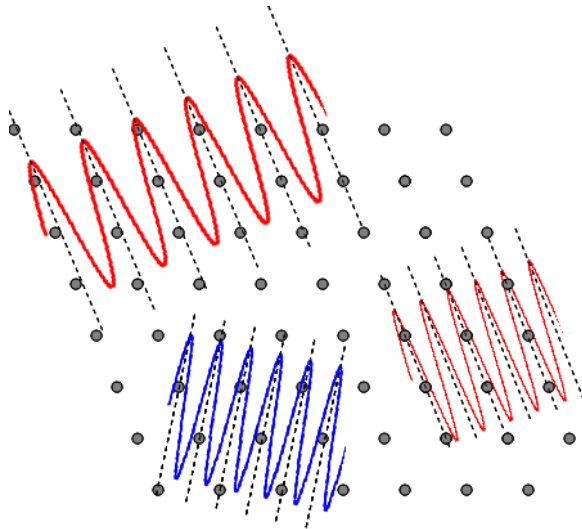

Figure 1. 2-Dimensional Bravais lattice with three waves of equal phase at all lattice points. The wavevector **k** of the top one (in red) is half that of the red one below it (but double wavelength). There is infinite number of waves that satisfy this condition

This condition can be expressed as: $e^{i\mathbf{K.R}} = 1$, where **R** represents any vector of the Bravais lattice.

A more mathematical definition of reciprocal space is as follows. If $\mathbf{a_1, a_2, a_3}$ are the unit cell vectors of the Bravais lattice (sometimes called "direct space"), then the unit cell vectors of the reciprocal space, $\mathbf{b_1, b_2, b_3}$ are:

$$\mathbf{b_1} = 2\pi \cdot \frac{\mathbf{a_2} \times \mathbf{a_3}}{\mathbf{a_1} \cdot (\mathbf{a_2} \times \mathbf{a_3})} ; \quad \mathbf{b_2} = 2\pi \cdot \frac{\mathbf{a_3} \times \mathbf{a_1}}{\mathbf{a_1} \cdot (\mathbf{a_2} \times \mathbf{a_3})} ; \quad \mathbf{b_3} = 2\pi \cdot \frac{\mathbf{a_1} \times \mathbf{a_2}}{\mathbf{a_1} \cdot (\mathbf{a_2} \times \mathbf{a_3})}$$

Notice that the denominator is simply the volume of the Bravais unit cell.
It is clear that $\mathbf{b_1}$ is perpendicular to $\mathbf{a_2}$ and $\mathbf{a_3}$, etc. etc. So that the following relations hold:

$\mathbf{b_1 . a_1} = 2\pi; \quad \mathbf{b_1 . a_2} = 0; \quad \mathbf{b_1 . a_3} = 0$
$\mathbf{b_2 . a_1} = 0; \quad \mathbf{b_2 . a_2} = 2\pi; \quad \mathbf{b_2 . a_3} = 0$
$\mathbf{b_3 . a_1} = 0; \quad \mathbf{b_3 . a_2} = 0; \quad \mathbf{b_3 . a_3} = 2\pi$

These relations will be very useful when discussing diffraction.

Exercises:
1. Draw the reciprocal lattice of the square, rectangular and hexagonal lattices in two dimensions.
2. What is the reciprocal lattice of a cubic bcc lattice ?
3. Same of an fcc lattice.

Miller Indices

It is clear from figure 1 that each family of parallel planes through the lattice points defines vectors **K** of the reciprocal space that are perpendicular to those planes. If d is the spacing between the nearest planes in the family it defines the longest wavelength. The length of K is then $= 2\pi n/d$, where n = 1,2,3,…   If **K** for n = 1 is expressed as a combination of the unit cell vectors **b₁, b₂, b₃**: $\mathbf{K} = h\mathbf{b_1} + k\mathbf{b_2} + l\mathbf{b_3}$, then the indices h,k,l are called the Miller Indices of the family of planes. Geometrically the indices can be found by considering the plane of the family that is closest to the origin. If this plane intercepts the **a₁, a₂, a₃** axis at positions x_1, x_2 and x_3 then $h:k:l = 1/x_1 : 1/x_2 : 1/x_3$

Wigner Seitz cell: is the volume in real space enclosed by planes perpendicular to the unit cell vectors through their mid-point.

First Brillouin Zone: Same definition as the Wigner Seitz cell but in reciprocal space.

Exercise: draw the two dimensional Wigner & Brillouin cells for the square, rectangular and hexagonal lattices.

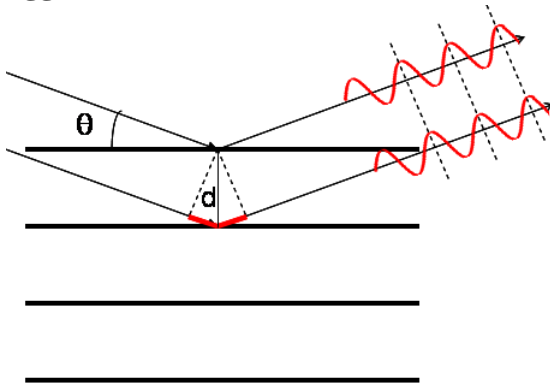**Bragg and Laue Diffraction conditions**

Figure 2. Illustration of the Bragg condition. Waves must reflect *in phase* from any pair of adjacent planes: therefore the difference in path length (red segments) must be a multiple of λ

Bragg law:
In 1913 Bragg found that x-rays were diffracted by crystals, i.e., the emerging x-rays travel only in very specific directions. He explained this by the interference of waves reflected from planes of atoms in the crystal.   For the reflected waves in consecutive planes to add *in phase* the difference in path length must be an integer of the wavelength:

$$2d.\sin\theta = m\lambda$$

So, for fixed values of d, θ, and λ, the condition cannot be fulfilled in general. To obtain diffraction one must adjust θ and /or λ. Adjusting θ leads to the method of the rotating crystal. Another way is to use powders of the crystal. There will always be a collection of crystallites with the right value of θ. The diffracted beams from these form a cone. Another possibility is to use "white" x-rays, i.e., x-rays that contain all wavelengths within a range. There will be always

one λ corresponding to a wave that diffracts from planes separated by distance d at the angle θ. This is used to find the orientation of a crystal.

Laue law:

   A more general proof of the diffraction condition is due to Laue who considered the scattered waves by any two points of the lattice (blue circles in the figure):

The incident and scattered wavevectors are **k** and **k'**, and the unit length vectors in these two
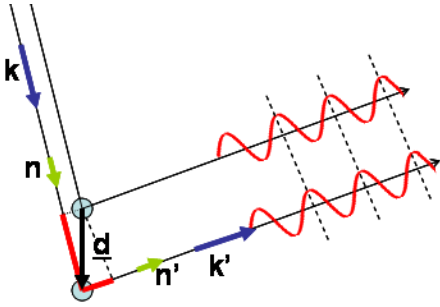

Figure 3. Illustration of the Laue condition. Waves must reflect *in phase* from any pair of lattice points: the difference in path length (red segments) must be a multiple of λ
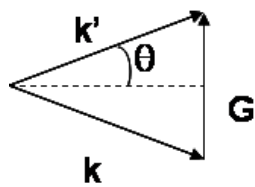
directions are **n** and **n'**.

$\mathbf{k} = 2\pi/\lambda.\ \mathbf{n}$ and $\mathbf{k'} = 2\pi/\lambda.\ \mathbf{n'}$

The vector **d** joins the two scattering centers. As in the Bragg case, the two scattered waves must be in phase for constructive interference:

$\mathbf{n.d} - \mathbf{n'.d} = m\lambda$ or $(\mathbf{k-k'}).\mathbf{d} = 2\pi m$

This relation must be valid *for all pairs of lattice points*, meaning that **d** is any Bravais lattice vector **R.**

$\Delta\mathbf{k.\ R} = 2\pi m$, is equivalent to $e^{i\Delta\mathbf{k.\ R}} = 1.$ We recognize this as the condition for $\Delta\mathbf{k}$ to be a vector of the reciprocal space. We thus see the intimate correlation between reciprocal space and diffraction.

If we designate by **G** a vector of the reciprocal space the condition $\Delta\mathbf{k} = \mathbf{G}$ is equivalent to $G/2 = k.\sin\theta$

Which by substituting $G = 2\pi/d$ and $k = 2\pi/\lambda$ leads to the Bragg law.

A very useful construction is the Ewald Sphere: A sphere with center at the end of vector **k** passing through the origin will intercept all points of the reciprocal space capable of giving diffraction peaks. In the drawing of the figure only one point is intercepted.

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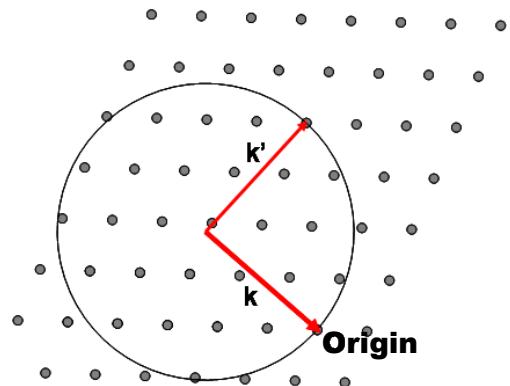
The scattering amplitude for particles interacting weakly with lattice atoms or electrons is:

$$\mathbf{A} = \sum_{j=0} \mathbf{f_j}(\theta) \cdot \mathbf{e^{ik.r_j}} \cdot \mathbf{e^{ik'(r-r_j)}} = \mathbf{e^{ik'r}} \cdot \sum_{j=0} \mathbf{f_j}(\theta) \cdot \mathbf{e^{i(k-k')r_j}}$$

The first factor is the amplitude for scattering in the direction θ. e^{ikr_j} is the amplitude of the incident wave at the position $\mathbf{r_j}$. The second term is the wave scattered from that position: $e^{ik'(r-r_j)}$

The assumption or weak scattering is because we neglect any other amplitude at the position r_j except the incident one. The other amplitudes, coming from scattered waves from the other positions are neglected assuming they are much weaker than the incident one. This is also called the *kinematic approximation.* For x-rays and high energy electrons this is a good approximation. For the low energy electrons used in LEED the approximation gives poor quantitative results. Even in that case however, the predictions of the kinematic approximation that are purely related to symmetry are still valid. For example if a given diffraction direction is forbidden, then the kinematic approximation would predict zero amplitude in that direction, which is correct. We will see examples of this below.
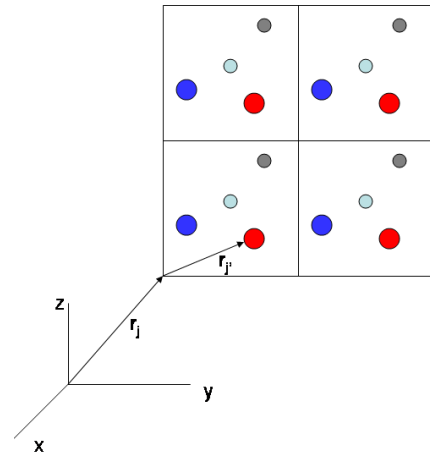
Structure factor:

Until now we have only considered scattering by lattice points. In general however the unit cell contains more than one atom, or, for x-rays, the electron distribution should be considered. The sum of scattered amplitudes from each scattering center inside the unit cell gives the structure factor S(Δ**k**):

$$S(\Delta k) = \sum_{j=0} f_j(\theta) \cdot e^{i\Delta k.r_j}$$

where $\mathbf{r_j}$ is the position of the scattering center and $f_j(\Delta\mathbf{k})$ is the scattering function which depends of the type of atom and scattering angle. The structure factor is an additional condition over the Laue condition and can result in the suppression of certain diffracted beams that otherwise satisfy the Lauer condition. For example, using the non-primitive cubic cell of a bcc crystal like W, the cell contains two identical atoms, one at the origin (0,0,0), the other at (1/2, 1/2, 1/2).

$S_{hkl} = f(\theta).[1 + e^{i\pi(h+k+l)}]$ where Δ**k** = h**b$_1$** + k**b$_2$** + l**b$_3$**

As we can see for S_{hkl} to be non-zero h+k+l must be even, which excludes the reflections (111), (210), etc.

Exercise: Find the structure factor conditions for: (a) an (a) an fcc crystal; (b) a cubic diamond structure

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**Atomic form factor due to the electron density distribution:**

In the previous paragraphs we have assumed the scattering centers to be the points of the lattice, or the group of point-like atoms forming the basis and giving rise to the structure factor. X-rays however are scattered by each individual electron. We take care of this by a similar procedure as in the structure factor by summing the scattered amplitudes, except that the electron distribution is a continuous function n(**r**) :

$$A(\Delta k) = \int dV.n(r).e^{ir.\Delta k} \quad = \sum_{j'}\sum_{j}\int dV.n_j(r-r_j-r_{j'}).e^{ir.\Delta k} \quad = \sum_{j}e^{ir_j.\Delta k}.\sum_{j'}f_{j'}(\theta).e^{ir_{j'}.\Delta k} \text{ and}$$

$$f_j(\theta) = \int dV.n_j(r-r_j-r_{j'}).e^{i(r-r_j-r_{j'}).\Delta k}$$

n_j(r) is the electron density function.

Exercise: calculate f_j for a uniform spherical distribution of charge.


$n_j(r) = n_o$ for $r < r_o$

Δk
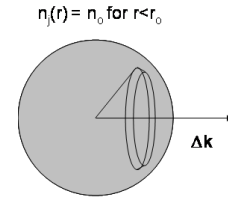
Diffraction from surfaces

Ewald construction

Like in the 3-dimensional case discussed above, the directions of the diffracted beams can be found easily with the help of the Ewald construction. The reciprocal lattice of points is drawn on the plane of the crystal surface. Then vertical lines are drawn perpendicular to the surface. A sphere is drawn with center at the extreme of a vector **k** (the incident wavevector) whose other end is at the origin of the 2-D reciprocal space. The intersection of the sphere with the vertical lines through the reciprocal lattice points marks the end of the wavevectors of the diffracted beams.

In the projected representation, the center of the Ewald circle is drawn at the position of the **K** vector (the surface projection of the incident wavevector), with a radius of k, the modulus of the incident wavevector. All reciprocal lattice points inside the circle correspond to diffracted beams and those outside to evanescent beams.

Perpendicular to the surface

Projection onto surface plane
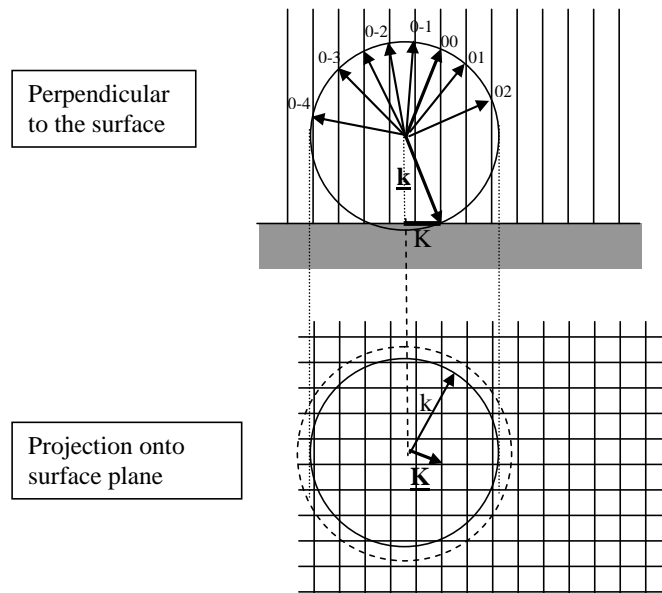
General formalism: Bloch theorem in 2 dimensional structures

The Bloch theorem, which is a consequence of the translational symmetry of the surface, implies that the interaction potential V(**r**) and the particle wavefunction ψ(**r**) can be written as sums over the reciprocal lattice:

$$V(\vec{r}) = \sum_{\vec{G}} V_{\vec{G}}(z) e^{i\vec{G}.\vec{R}} \qquad (1)$$

and

$$\psi(\vec{r}) = \sum_{\vec{G}} \psi_K(z) e^{i(\vec{K}+\vec{G})\vec{R}} = \sum_{\vec{G}} \psi_K(z) e^{i\vec{K}_G \vec{R}} \qquad (2)$$

We have written **r** = (z, **R**), where the z coordinate is separated from the x,y coordinates, represented by the vector **R**. The **G**'s are the 2-dimensional reciprocal lattice vectors and **K$_G$** = **K**+**G**, which expresses the conservation of crystal momentum parallel to the surface. In the following we will always use capital letters for surface magnitudes (K for momentum, R for the spatial coordinate), and small letters with a sub-z for their normal components.

The schematic drawing illustrates the geometry of the diffracted beams and the vector magnitudes associated. The beams are classified as follows:
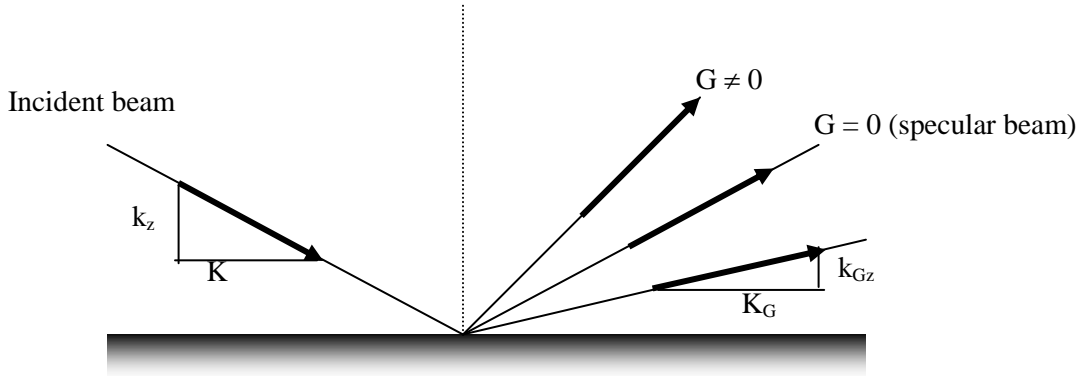
(1) **G** = 0. This contains the incident and specularly reflected beams. The asymptotic form of the wave function corresponds to two plane waves:

$$\psi_0(\infty) = e^{-ik_z z} + R_o e^{ik_z z} \qquad (3)$$

the first one is for the incident beam, the second for the reflected beam. The value of the amplitude R$_o$ must be found by solving the Schrödinger equation.

(2) Real diffracted beams. Here **G** ≠ 0, and the following condition is fulfilled:

$$k_{Gz}^2 = k^2 - (\vec{K} + \vec{G})^2 > 0 \qquad (4)$$

The asymptotic form of the wavefunction is:

$$\psi_{\vec{G}}(\infty) = R_{\vec{G}} e^{ik_{G_z} \cdot z} \qquad (5)$$

Again the R_G's are to be found by solving the Schrödinger equation. There is a finite number of real diffracted beams.

(3) Evanescent beams. Again $\mathbf{G} \neq 0$, but now

$$k_{G_z}^2 = k^2 - (\vec{K} + \vec{G})^2 < 0 \quad (6)$$

For these beams, the wavefunction is exponentially decaying:

$$\psi_{\vec{G}}(\infty) = R_{\vec{G}} e^{-k_{G_z} \cdot z} \qquad (7)$$

There is only amplitude near the surface. The particles move parallel to the surface until they are scattered back into one of the real beams, by exchanging a G vector with the lattice.

The dashed circle in the Ewald construction shown above corresponds to resonances with bound states of the attractive well $V_0(z)$. Its radius is equal to $(k^2 + k_n^2)^{1/2}$, where $-k_n^2$ is the energy of a bound state. When an evanescent beam fulfills the condition:

$$k_{G_z}^2 = k^2 - (\vec{K} + \vec{G})^2 = -k_n^2 \qquad (8)$$

a resonance occurs called Lennard-Jones resonance. In that case the particle can be trapped on the surface for a much longer time before being scattered back into a real beam. Such resonance effects can be important in chemisorption.